Transfer Hydrogenation and Transfer Hydrogenolysis. X. Selective Hydrogenation of Methyl Linoleate by Indoline and Isopropyl Alcohol

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ABSTRACT AND SUMMARY

The selective hydrogenation of methyl linoleate was studied using indoline and isopropyl alcohol as hydrogen sources. Many transition metal compounds and metallic palladium were examined as catalysts. High selectivity to monoenes and little formation of *trans* isomers were realized under mild conditions in some reaction systems. For example, the system in which isopropyl alcohol and $RuCl_2(PPh_3)_3$ were used as hydrogen donor and catalyst was excellent. Also in the hydrogen transfer from indoline to the linoleate catalyzed by $PdCl_2$ and $(NH_4)_2PdCl_4$, high selectivity was realized. In the $RuCl_2(PPh_3)_3$-isopropyl alcohol, $(NH_4)_2PdCl_4$-indoline and $PdCl_2$-indoline system, methyl *cis-trans* conjugated octadecadienoate was reduced rapidly with complete selectivity, whereas the same hydrogen transfer systems resulted in little if any reaction with methyl oleate. High selectivity in the reduction of linoleate is presumed to be realized through prior conjugation of the substrate.

INTRODUCTION

Much work has been carried out on the partial hydrogenation of oils to improve the oxidative stability and the flavor of edible vegetable oils and the properties of raw materials for soap. In the hydrogenation, the formation of saturated products and *trans* and positional double bond isomers are undesirable reactions. In most studies on the hydrogenation of oils, molecular hydrogen has been used as the hydrogen source and relatively few studies of the hydrogen transfer from organic compounds [transfer hydrogenation (1)] have been reported (2). As for the transfer hydrogenation of oils, hydrogen transfer from alcohol has been reported to be catalyzed by metallic nickel (3), $PtCl_2(AsPh_3)_2 + SnCl_2 \cdot 2H_2O$ (4), $PdCl_2(PPh_3)_2 + SnCl_2 \cdot 2H_2O$ (5), $Pd(CN)_2(PPh_3)_2$ (5), and nickel acetylacetonate (6). Further, there has been one report that monoenes are formed by heating methyl *cis*-9,*cis*-12-octadecadienoate and $NiX_2(PPh_3)_2$ (X = Br or I) in tetrahydrofuran or benzene under nitrogen pressure (7). Generally, the selectivity to monoenes is excellent but the formation of *trans* isomers and the migration of double bonds are extensive in these transfer hydrogenations.

In the course of basic studies of transfer hydrogenation of olefins (8-12), we found several active hydrogen donors and catalysts. This study was undertaken to investigate the selective transfer hydrogenation of methyl linoleate under mild conditions in more detail.

EXPERIMENTAL PROCEDURE

Materials

Methyl linoleate was prepared from safflower oil (13). Conjugated methyl octadecadienoates were prepared from methyl linoleate by the reaction catalyzed with potassium hydroxide (14). Methyl oleate was prepared by esterification of refined oleic acid with methyl alcohol. Metallic palladium and salt catalysts were purchased and used without purification. Complex catalysts were synthesized by the methods previously reported (8-12). The hydrogen donors and the solvents were purified by distillation.

An Example of Transfer Hydrogenation

Methyl linoleate (59 mg. 0.20 mmol), indoline (48 mg, 0.40 mmol), and a catalyst (0.02 mmol) were put into a pyrex glass tube, and the total volume of the solution was made 1.0 ml by the addition of toluene as a solvent. The tube was sealed under vacuum using liquid nitrogen and a vacuum line. The sealed tube was heated for 3 hr with continuous oscillation in a polyethylene glycol bath kept at the designated temperature ± 1 C. The reaction mixture was submitted to gas liquid chromatographic (GLC) analysis which was performed at 220 C, using 15 μl of dibenzyl ether as an internal standard. A 2 m x 6 mm stainless steel column packed with 12% diethylene glycol succinate on Diasolid L was used. Volatile compounds were removed from the reaction mixture under reduced pressure. The residue was dissolved in carbon tetrachloride and then submitted to IR analysis to measure the amount of *trans* double bonds. Although the residue contained dibenzylether, indoline, and indole, it was confirmed that they did not influence the IR analysis.

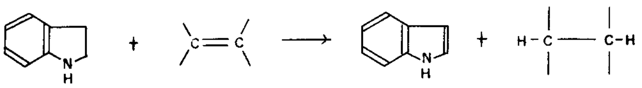
Other transfer hydrogenations were carried out in a similar way.

RESULTS

As hydrogen donors, indoline and isopropyl alcohol were examined, since the amine showed the highest hydrogen donating ability in the transfer hydrogenation of olefins catalyzed by $RhCl(PPh_3)_3$ (9) and Pd-carbon (10), and the alcohol has been used in many studies as a representative hydrogen donor (3,6,11,12,15).

Hydrogen Transfer from Indoline

It was confirmed that in the hydrogen transfer from indoline to olefins, the stoichiometric amount of indole and paraffins were formed and the following reaction proceeded without side reactions (9,10). In the catalytic reaction between indoline and methyl linoleate, monoenes, stearate, isomerized dienoates and indole were formed (Equation 1).



The total amount of these C_{18}-esters, including residual linoleate, in the reaction mixtures was found to be equal to the amount of the initial linoleate within experimental error, except for the cases in which stannous chloride was added. The amount of the indole formed also equaled the theoretical within experimental error when stannous

TABLE I

Hydrogen Transfer from Indoline to Methyl Linoleate[a]

Catalyst	Reaction temp (C)	Yield of products (%)			Conv.[e] (%)	Select.[f] (%)	*trans* (%)	
		S[b]	M[c]	CD[d]			A[g]	B[h]
50% Pd-asbestos	80	12	77	0	89	86	48	48
	100	49	51	0	100	51	23	45
Pd-black	80	29	55	0	84	66	41	47
	100	43	57	0	100	57	29	51
5% Pd-carbon	80	15	47	0	62	76	47	38
	100	28	56	0	84	67	48	56
	120	33	67	0	100	67	45	67
$RhH(PPh_3)_4$	100	32	53	0	85	62	42	51
	120	24	76	0	100	57	29	51
$RuH_2(PPh_3)_4$	100	15	66	0	81	82	87	84
	120	18	66	0	84	79	78	80
$RuCl_2(PPh_3)_3$	100	14	65	0	79	82	94	88[i]
	120	83	27	0	100	27	10	37[i]
$RhCl_3 \cdot 2H_2O$	120	17	59	0	75	78	71	65
	140	20	61	0	81	75	55	56
K_2PtCl_4[j]	120	26	37	0	63	58	15	13
	140	39	46	0	85	54	29	38
$PdCl_2$[j]	120	0	41	0	41	100	41	26
	140	0	57	0	57	100	52	36
$IrCl_3$[j]	120	17	23	0	40	57	16	11
$(NH_4)_2PdCl_4$[j]	120	0	32	0	32	100	20	12
	140	0	60	0	60	100	44	31
$RuH_2(CO)(PPh_3)_3$	140	15	33	19	48	68	64	65
$RhBr(PPh_3)_3$	140	6	39	30	45	87	15	16
$RhCl(PPh_3)_3$	140	0	31	22	31	100	18	14
$PdBr_2$	140	0	16	0	16	100	0	0
$PdCl_2(PPh_3)_2 + SnCl_2 \cdot 2H_2O$[k,l]	140	0	15	16	15	100	26	17

[a] Methyl linoleate (0.2 M), indoline (0.4 M) and the designated catalyst were heated in toluene for 3 hr. The concentration of catalysts was 10 g/liter for metallic palladium catalysts and 20 mM for other catalysts.

[b] S = methyl stearate.

[c] M = monoenes.

[d] CD = conjugated dienes.

[e] Conv. = conversion, which is given by $\dfrac{[\text{Stearate}] + [\text{Monoenoates}]}{[\text{C}_{18}\text{-esters}]}$ x 100.

[f] Select. = selectivity, which is given by $\dfrac{[\text{Monoenoates}]}{[\text{Stearate}] + [\text{Monoenoates}]}$ x 100.

[g] *trans* percent (A) = $\dfrac{[\textit{trans}\text{ isomers as elaidate}]}{[\text{C}_{18}\text{-esters}]}$ x 100 by IR analysis.

[h] *trans* percent (B) = $\dfrac{[\textit{trans}\text{ isomers as elaidate}]}{[\text{Monoenes}] + [\text{Nonconjugated dienes}] \times 2}$ x 100.

The compositions used in notation e,f,g, and h were determined by gas liquid chromatographic (GLC) analysis.

[i] Good reproducibility was confirmed.

[j] This catalyst did not dissolve completely.

[k] $SnCl_2 \cdot 2H_2O$ (0.2 M) was added.

[l] A resinous compound was formed and the amount of C_{18}-esters diminished.

chloride was not used. We examined three forms of metallic palladium and thirty–four salt or complex catalysts including six which have been reported in the transfer hydrogenation of methyl linoleate (4,6,7) and soybean oil methyl ester (5). The solubility of transition metal salts and complexes seemed to be greatly enhanced by the presence of the hydrogen acceptor and the hydrogen donor, but a considerable number of catalysts did not dissolve completely. The transfer hydrogenations were carried out by heating methyl linoleate (0.2 M), indoline (0.4 M), and a slat catalyst or a complex catalyst (20 mM) or a metallic palladium (10 g/liter) in toluene for 3 hr. The reaction vessel was continuously oscillated during the hydrogenation. At these concentrations, the amount of metallic palladium from Pd-black, 50% Pd-asbestos, and 5% Pd-carbon is about 4.7, 2.4, and 0.23 times as much as that in palladium complexes, respectively. The reaction mixtures were submitted to GLC analysis and then to IR analysis to estimate the amount of isolated *trans* double bonds as elaidate by the peak at 968 cm^{-1} (16). As it was difficult to draw a base line precisely on the peak, the experimental errors in the estimation of the *trans* bonds are presumed to be considerably large (17). The results are given in Table I, in which conversion shows the total yield of the hydrogenation products and selectivity shows the percentage of monoenes in the hydrogenation products. *trans* Percent (A) represents the supposed yield of *trans* isomers based on elaidate, and *trans* percent (B) represents the percentage of isolated *trans* double bonds in all the isolated double bonds in the reaction mixtures. The former notation has been used in most reports on the hydrogenation of oils but the latter seems to be more useful in scientific discussions. Table I contains only cases in which the conversion was higher than 15% in the reaction at 140 C. The reactions catalyzed by metallic palladium occurred under the mildest condition. As some of the salt and complex catalysts did not dissolve completely, their real activity could not be

TABLE II

Hydrogen Transfer from Isopropyl Alcohol to Methyl Linoleate[a]

Catalyst	Reaction temp (C)	Yield of products (%)			Conv.[b] (%)	Select.[b] (%)	*trans* (%)	
		S[b]	M[b]	CD[b]			A[b]	B[b]
$RuH_2(PPh_3)_4$	120	28	57	0	85	67	17	20
	80[c]	45	39	0	84	47	23	32
	80[d]	0	50	17	50	100	trace	trace
$RhH(PPh_3)_4$	120	20	59	0	80	75	34	33
	60[c]	0	33	20	33	100	25	20
	70[d]	40	60	0	100	60	trace	trace
$RuCl_2(PPh_3)_3$[e]	120	0	59	15	59	100	trace	trace
	140	0	68	15	68	100	trace	trace
	120[c]	0	76	0	76	100	90	73
$RhCl_3 \cdot 2H_2O$[e]	120	0	30	27	30	100	27	16
	140	0	44	0	44	100	24	15
$PdCl_2(PPh_3)_2 + SnCl_2 \cdot 2H_2O$[f,g]	140	0	29	30	29	100	36	32
$PdBr_2$	140	0	26	15	26	100	trace	trace
$PtCl_2(AsPh_3)_2 + SnCl_2 \cdot 2H_2O$[f,g]	140	0	18	22	18	100	69	50

[a] Methyl linoleate (0.2 M), isopropyl alcohol (0.4 M) and the designated catalyst (20 mM) were heated in toluene for 3 hr.

[b] Notations in this table are same as those in Table I.

[c] This reaction was carried out in a mixture of toluene and isopropyl alcohol (1:1).

[d] This reaction was carried out in isopropyl alcohol.

[e] This catalyst did not dissolve completely.

[f] $SnCl_2 \cdot 2H_2O$ (0.2 M) was added.

[g] A resinous compound was formed and the amount of C_{18}-esters diminished.

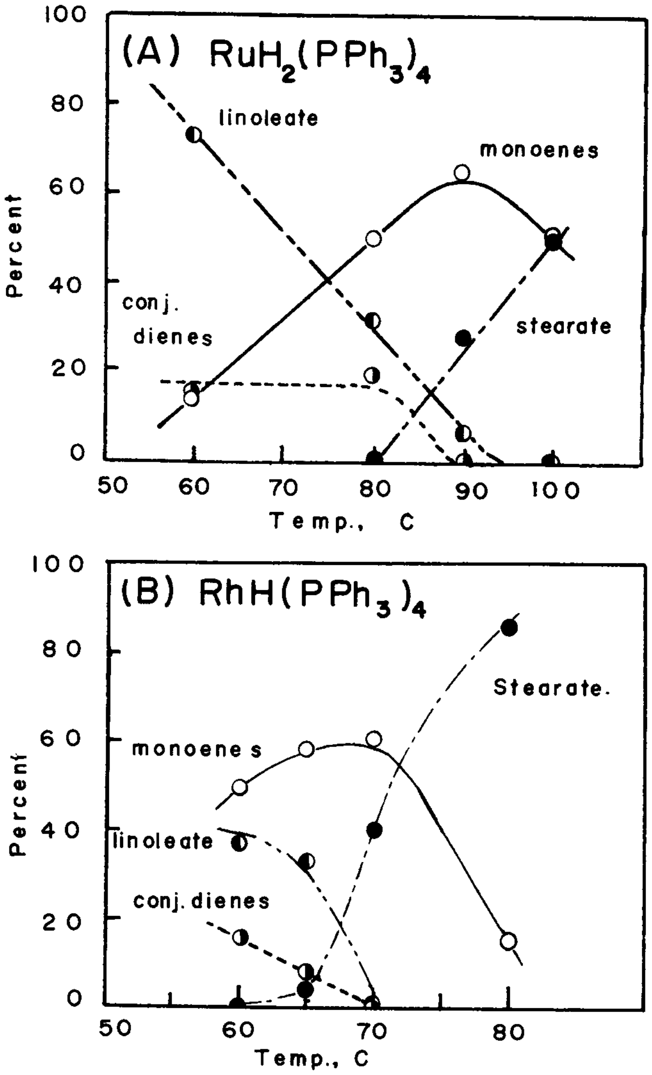


FIG. 1. Dependence of the composition of C_{18}-esters on temperature: linoleate (0.2 M) was heated in isopropyl alcohol in the presence of (A) $RuH_2(PPh_3)_4$ (20 mM) at 60, 80, 90, 100 C and of (B) $RhH(PPh_3)_4$ at 60, 65, 70, 80 C.

determined. The apparent activity of the soluble catalysts expressed by conversion decreased in the following order; $RhH(PPh_3)_4 > RuH_2(PPh_3)_4 \approx RuCl_2(PPh_3)_3 > RhCl_3 \cdot 2H_2O \approx K_2PtCl_4 > PdCl_2 \approx IrCl_3 \approx (NH_4)_2PdCl_4 > RuH_2(CO)(PPh_3)_3 \approx RhBr(PPh_3)_3 > RhCl(PPh_3)_3 > PdBr_2 \approx PdCl_2(PPh_3)_2 + SnCl_2 \cdot 2H_2O$ (0.2 M).

$NiCl_2(PBu^n_3)_2$, $NiBr_2(PBu^n_3)_2$, $NiBr_2(PPh_3)_2$, $NiI_2(PPh_3)_2$, $CuBr_2$, $RhCl(CO)(PPh_3)_2$ and $PtCl_2(AsPh_3)_2 + SnCl_2 \cdot 2H_2O$ also catalyzed the hydrogenation, but the conversion was lower than 15% in the reaction at 140 C. $CoCl_2$, $Ni(acac)_2$, CuBr, $PdCl_2(PPh_3)_2$, $PdCl_2(PBu^n_3)_2$, $Pd(CN)_2(PPh_3)_2$, $PtCl_2(PPh_3)_2$, $PtCl(PPh_3)_2 + SnCl_2 \cdot 2H_2O$ and K_2PtCl_6 showed no activity on the hydrogenation. In the reaction system containing stannous chloride, resinous compounds also were formed and the accuracy of the analysis was greatly lowered. Perhaps Friedel-Crafts type reaction might occur in these systems. Further, it was revealed that all the catalysts which had been reported to be active in the transfer hydrogenation of oils (4-7) exhibited very little or no activity under our reaction conditions. The selectivity varied with the catalysts and decreased with an increase in conversion. In the reaction catalyzed by $PdCl_2$ and $(NH_4)_2PdCl_4$, the selectivity was 100% at a conversion of about 60%. In the reaction catalyzed by metallic palladium, $RhH(PPh_3)_4$, $RuCl_2(PPh_3)_3$, $RuH_2(PPh_3)_4$ and $RhCl_3 \cdot 2H_2O$, it was 66-89% at conversions of 79-89%.

Although the experimental errors of the *trans* percents were considerably large as described before, the results in Table I show the general tendency that the *trans* percent (A) increased at first and then decreased as the conversion increased, and that the one (B) increased linearly. The former fact shows that a maximum exists in the amount of the isolated *trans* double bonds formed except for highly selective catalyst systems whereas the latter demonstrates that the percentage of *trans* bonds for all isolated double bonds steadily increases as the hydrogenation proceeds. Generally speaking, the metallic palladium, $PdCl_2$, $(NH_4)_2PdCl_4$ and K_2PtCl_4 showed less tendency to catalyze the formation of *trans* bonds than the ruthenium and rhodium complexes. Conjugated dienes were not observed in these reactions, except for the one catalyzed by $RhCl(PPh_3)_3$, $RuH_2(CO)(PPh_3)_3$, $RhBr(PPh_3)_3$ and

TABLE III

Transfer Hydrogenation of Conjugated Methyl Octadecadienoate[a]

Catalyst	Hydrogen donor	Reaction temp (C)	Yield of Products (%)				Conv.[b] (%)	Select.[b] (%)	*trans* (%)	
			S[b]	M[b]	c-t[c]	t-t[d]			A[b]	B[b]
$(NH_4)_2PdCl_4$[e]	Indoline	140	0	100	0	0	100	100	79	79
5% Pd-carbon		100	27	73	0	0	100	73	44	60
$RuH_2(PPh_3)_4$		100	61	39	0	0	100	39	23	59
$RhH(PPh_3)_4$		100	47	50	0	0	97	52	31	55
$PdCl_2$[e]		120	0	87	0	9	81	100	48	52
$RhCl_3 \cdot 2H_2O$[e]		120	12	62	17	9	74	83	22	35
K_2PtCl_4[e]		120	18	33	41	7	51	65	8	24
$RuH_2(PPh_3)_4$	i-PrOH	120	54	44	0	0	98	45	30	62
$RhH(PPh_3)_4$		120	39	58	0	0	97	60	42	66
$RuCl_2(PPh_3)_3$[e]		140	0	96	0	4	96	100	51	53
$PdBr_2$		140	0	36	15	49	36	100	10	28
$RhCl_3 \cdot 2H_2O$[e,f]		140	0	0	60	40	0			

[a] Conjugated methyl octadecadienoates (0.2 M), the designated hydrogen donor (0.4 M) and the designated catalyst were heated in toluene for 3 hr. The concentration of catalysts was same as in Table I.

[b] Notations in this table were same as in Table I.

[c] *cis-trans* conjugated methyl octadecadienoates.

[d] *trans-trans* conjugated methyl octadecadienoates.

[e] This catalyst did not dissolve completely.

[f] Good reproducibility was confirmed.

TABLE IV

Transfer Hydrogenation of Methyl Oleate[a]

Catalyst	Hydrogen donor	Reaction temp (C)	Yield of stearate (%)[b]	*trans* (%)	
				A[c]	B[c]
$(NH_4)_2PdCl_4$	Indoline	140	0	14	14
$PdCl_2$		120	0	4	4
$RhH(PPh_3)_4$		100	33	11	42
$RhCl_3 \cdot 2H_2O$		140	35	25	38
$RuCl_2(PPh_3)_3$		100	38	46	74
5% Pd-carbon		100	49	12	23
$RuH_2(PPh_3)_4$		100	76	17	70
$RuCl_2(PPh_3)_3$	i-PrOH	140	0	24	24
$RhH(PPh_3)_4$		120	35	37	57
$RuH_2(PPh_3)_4$		120	74	trace	trace

[a] Methyl oleate (0.2 M), the designated hydrogen donor (0.4 M) and the designated catalyst were heated in toluene for 3 hr. The concentration of catalysts was same as in Table I.

[b] $$\text{Yield of stearate} = \frac{[\text{Stearate}]}{[\text{Stearate}] + [\text{Monoenes}]} \times 100.$$

[c] Notations in this table were same as in Table I.

$PdCl_2(PPh_3)_2 + SnCl_2 \cdot 2H_2O$.

$PdCl_2$ and $(NH_4)_2PdCl_4$ may be regarded as fairly good catalysts, because high selectivity and relatively low formation of *trans* isomers are realized, although the conversions are not high.

Hydrogen Transfer from Isopropyl Alcohol

It is well known that isopropyl alcohol gives olefins hydrogen to yield acetone (11,12,15), but it is inferred that the hydrogen-donating power of the alcohol is lower than indoline (9,10). Therefore, the hydrogen transfer from isopropyl alcohol was examined only with those catalysts which were active in the reaction with indoline or had been reported to be active in the transfer hydrogenation of oils. The reaction conditions were similar to those used in the reaction with indoline. As shown in Table II, the catalytic activity decreased in the order $RuH_2(PPh_3)_4 > RhH(PPh_3)_4 > RuCl_2(PPh_3)_3 > RhCl_3 \cdot 2H_2O > PdCl_2(PPh_3)_2 + SnCl_2 \cdot 2H_2O \approx PdBr_2 > PtCl_2(AsPh_3)_2 + SnCl_2 \cdot 2H_2O$.

Pd-black, Pd-asbestos, Pd-carbon, $PdCl_2$, $(NH_4)_2PdCl_4$ and $Pd(CN)_2(PPh_3)_2$ catalyzed the reduction by the alcohol, but the conversions were less than 15% even at 140 C.

$NiCl_2(PBu^n_3)_2$, $NiBr_2(PPh_3)_2$, $NiBr_2(PBu^n_3)_2$, $NiI_2(PPh_3)_2$, $CuBr_2$, $RuH_2(CO)(PPh_3)_3$, $RhCl(PPh_3)_3$, $RhBr(PPh_3)_3$, $RhCl(CO)(PPh_3)_2$, $IrCl_3$ and K_2PtCl_4 showed no activity in the reactions at 140 C. When stannous chloride was used, resinous compounds were formed and the amount of the C_{18}-esters were reduced considerably. $RuCl_2(PPh_3)_3$ was found to be an excellent catalyst because the selectivity was 100% and *trans* isomers were not detected even in the reaction of 68% conversion. It is noteworthy that the *trans* percent (B) did not exceed 33% in any case in the absence of stannous chloride. Generally speaking, the reduction by isopropyl alcohol showed lower conversion, higher selectivity, and lower *trans* percents than the hydrogenation by indoline.

Reaction in Isopropyl Alcohol

It was expected that the reactions in a neat hydrogen donor would proceed under milder conditions and the product distribution might be improved. However, in the reactions in which isopropyl alcohol was used as a hydrogen donor and solvent, the catalysts did not dissolve completely. The reaction catalyzed by $RhH(PPh_3)_4$, $RuH_2(PPh_3)_4$, and $RuCl_2(PPh_3)_3$, proceeded at lower temperatures than the ones in toluene (Table II), but in the reactions catalyzed by $RhCl_3 \cdot 2H_2O$, $PdBr_2$, $PtCl_2(AsPh_3)_2$ + $SnCl_2 \cdot 2H_2O$ and Pd-carbon, the conversion at 100 C was less than 15%. It is notable that no resinous product was formed in the reaction in the alcohol catalyzed by $PtCl_2(AsPh_3)_2$ + $SnCl_2 \cdot 2H_2O$, but the conversion was negligible.

To promote the solubility of the catalysts, an isopropyl alcohol-toluene mixture (1:1) was used instead of the neat alcohol (Table II). In this system, $RhH(PPh_3)_4$ and $RuH_2(PPh_3)_4$ dissolved completely, but $RuCl_2(PPh_3)_3$ did not. Generally speaking, the composition of the products from this mixed solvent system was similar to the straight isopropyl alcohol system.

In the reaction of $RhH(PPh_3)_4$ and $RuH_2(PPh_3)_4$ in the alcohol or the mixed solvent, the conversion and selectivity varied with reaction temperatures. As examples, the reaction in the alcohol catalyzed by $RhH(PPh_3)_4$ and the one catalyzed by $RuH_2(PPh_3)_4$ are shown in Figure 1. The otpimum temperatures seems to be 65 C in the former and 80 C in the latter.

Solvent Effect

The distribution was not so changed by using chlorobenzene, tetrahydrofuran, or hexane instead of toluene, in the hydrogen transfer from indoline and isopropyl alcohol catalyzed by $RuH_2(PPh_3)_4$. Perhaps these solvents do not participate in the transition state during the hydrogen transfer steps.

Transfer Hydrogenation of Conjugated Dienes and Methyl Oleate

The transfer hydrogenation of conjugated methyl octadecadienoates and methyl *cis*-octadecenoate was carried out under the reaction conditions which had given good conversions in the corresponding transfer hydrogenation of methyl linoleate. The conjugated dienes were shown to consist of 90% of *cis-trans* and 10% of *trans-trans* isomers by GLC analysis.

Except for the case of the reaction in isopropyl alcohol catalyzed by $RhCl_3 \cdot 2H_2O$, the conversions of the conjugated dienes were higher than those of linoleate under similar reaction conditions (Table III). In addition, complete selectivity was obtained with the systems $(NH_4)_2PdCl_4$-indoline, $PdCl_2$-indoline and $RuCl_2(PPh_3)_3$-isopropyl alcohol. This means that all the systems which were highly selective in the reduction of methyl linoleate showed the same selectivity in the hydrogenation of the conjugated dienes, and vice versa.

The reason why $RhCl_3 \cdot 2H_2O$ did not catalyze the hydrogen transfer from alcohol to the conjugated dienes is not clear, in view of its success with methyl linoleate.

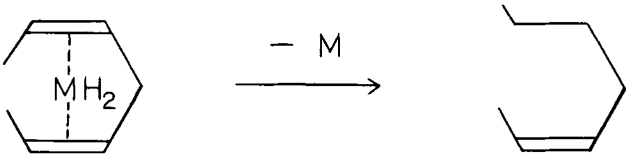
In the system of $(NH_4)_2PdCl_4$-indoline, $PdCl_2$-indoline, and $RuCl_2(PPh_3)_3$-isopropyl alcohol, the hydrogenation of methyl oleate to stearate was not observed and the isomerization to *trans* isomers was not extensive (Table IV). These results indicate that the high selectivity and the low *trans* percent observed in these systems is due at least partly to the inertness of the monoenoates formed in the selective reduction of the dienes. In any system in which the selectivity is not complete in the reduction of the nonconjugated and the conjugated dienes, the formation of the stearate was observed in the transfer hydrogenation of the oleate and vice versa.

DISCUSSION

Although the mechanisms of the transfer hydrogenation of linoleate may differ, depending on the combination of hydrogen donors and catalysts, we will try to discuss the mechanism to describe the high *cis*-monoene selectivity for the $(NH_4)_2PdCl_4$-indoline, $PdCl_2$-indoline, and $RuCl_2(PPh_3)_3$-isopropyl alcohol systems.

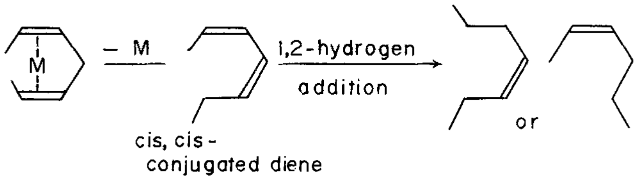
Almost all studies on the selective hydrogenation of oils have inferred that the high selectivity to monoenes is realized through prior conjugation of polyenes (2). In our reduction systems, too, the same mechanism seems to function, because the conjugated dienes, which had been prepared from linoleate, were hydrogenated more rapidly and a close correlation with selectivity was observed between the reduction of linoleate and that of the conjugated dienes. Further, at least in those reactions of high selectivity, the fact that conjugated dienes were not detected in many cases may be explained by the inference that the conjugated dienes once formed were rapidly reduced to monoenes.

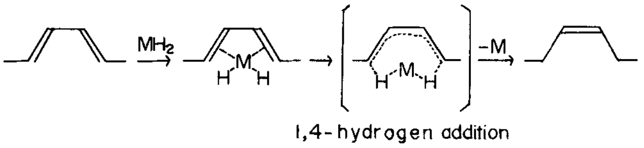
However, the possibility that linoleate is selectively hydrogenated prior conjugated, for example, through the coordination on dihydride species, cannot be ruled out a priori (Equation 2).



To realize high selectivity, it is also necessary that the monoenes formed be inert to further reduction. This criterion was satisfied in the three systems being discussed.

Of the mechanisms to realize both high selectivity and low *trans* percents, the following two may be considered: one is 1,2-hydrogen addition which follows the conjugated to *cis,cis,*-dienes (5) (Scheme I) and the other is the concerted 1,4-hydrogen addition to the conjugated diene which has coordinated with a catalytic dihydride species by chelation (2,5,18) (Scheme II).





As described earlier, with the three systems under consideration, the following results were obtained. (a) Linoleate gave mainly *cis*-monoenes and the reduction proceed via conjugation of the nonconjugated *cis,cis*-diene. (b) *cis,trans*-Conjugated dienes yielded monoenes, 50-80% of which were *trans* isomers. (c) Methyl oleate (*cis*-monoene) was for the most part unchanged and this result demonstrated that the *trans* isomers formed in the reduction of *cis,trans*-conjugated dienes were obtained by the isomerization of the *cis* isomer produced in the hydrogenation step of the dienes. According to Scheme II, any conjugated diene should give a *cis* isomer. This result was not obtained at least in the hydrogenation of *cis,trans*-conjugated dienes. Therefore, Scheme I seems to be more reasonable than Scheme II in the completely *cis*-monoene selective systems.

The fact that the product distributions in the transfer hydrogenations varied with the hydrogen donor may be explained by one of the following: (a) the hydrogen donors participate in the transition state in the transfer of hydrogen from the catalysts to methyl linoleate or the other C_{18}-unsaturated esters; (b) they take part in the transition state during the isomerization of linoleate which occurs prior to hydrogenation, influencing the structure of isomers, which in turn, determine the final product distribution; (c) the hydrogen-donating ability of the hydrogen donors affects the relative rates of the isomerizations and the hydrogenation, which decide the final product distribution, though the hydrogen donors and the dehydrogenated donors are not involved in the transition states of the hydrogenation and the isomerizations. The last explanation may be consistent with the report that the product distribution varies with hydrogen pressure in competitive hydrogenation and isomerization (19). However, to decide which mechanism is most plausible, further study is needed and is now in progress.

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